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Physical properties of hemicellulose films from sugarcane bagasse

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Abstract

Agricultural waste such as sugarcane bagasse can be obtained in large quantities from sugar and alcohol industries. Normally sugarcane bagasse has been used as a fuel to generate power of sugar mill. However, a huge quantity of the remaining bagasse is not used and burnt in the fields which can cause environmental problems. In recent years, many researchers show interest in utilization of agricultural waste to value-added products. Sugarcane bagasse contains about 33.5% hemicelluloses, which can be further utilized to produce other useful applications. The applications of material from hemicelluloses that have been identified include packaging films, food coatings, cationic biopolymers, hydrogels and biomedical uses. The objective of this study is to develop films from sugarcane bagasse hemicelluloses and to characterize the physical properties of hemicelluloses films. Biodegradable films were developed from hemicelluloses from sugarcane bagasse which was extracted using alkali extraction method. The alkali extraction of hemicelluloses was carried out at optimum condition with 3% NaOH concentration, temperature at 55°C and pH 5.5. Four different volumes of ethanol and acetic acid solution were added to the supernatant to produce hemicelluloses. The hemicelluloses A, B, C and D were obtained from 85ml of ethanol solution containing 10% acetic acid, 85 ml of cold ethanol solution, 4 volumes of ethanol, and 2 volumes of ethanol solution containing 0.2 volumes acetic acid, respectively. Films A, B, C and D were produced by casting the film-forming solutions, followed by solvent evaporation at a temperature of 40°C and relative humidity of 52.9% in a controlled environment. The physical properties such as thickness, solubility, water vapor transfer rate, surface structure and color of the hemicelluloses films from sugarcane bagasse were investigated. All the extracts of hemicelluloses produced self-supporting films with thickness ranging from 0.13 mm - 0.15 mm, 36.9 - 67.1% solubility in water, 250.4 - 483.3 g/(m^2.day) water vapor transfer rate (WVTR) and 0.31 - 1.72 MPa of tensile strength. The surface structure and color of the hemicelluloses films A, B, C and D are different probably due to the content of lignin in each of the film. This study suggests that hemicellulose of sugarcane bagasse has a good potential for production of biodegradable films for certain applications.

Keywords: Sugarcane bagasse; hemicellulose films; physical properties

1. Introduction

Sugarcane bagasse is a residue produced in large quantities by sugar industry and alcohol industries. About 54 million dry tons of bagasse is produced annually throughout the world [1]. In recent years, there has been an increasing trend towards more efficient utilization of agro-industrial residues, such as sugarcane bagasse, as raw materials for industrial applications. Bagasse is a rich source of not only cellulose, but also hemicellulose, represented by L-arabino-(4-O-methyl-D-glucurono)-D-xylan [2]. Hemicelluloses are polymer of xylose, galactose, mannose, arabinose, other sugars and their uronic acids. These are usually classified according to the sugar residue present. The hemicelluloses rank next to cellulose as the most abundant natural carbohydrate polymer in biosphere. They are

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present in all layers of plant cell wall but are concentrated mainly in primary and secondary layers where they occur closely associated with cellulose and lignin. Unlike cellulose, hemicelluloses are not chemically homogenous. Hardwood hemicelluloses contain mostly xylans, whereas softwood hemicelluloses contain mostly glucomannans [3].

Food packaging is concerned with the preservation and protection of all types of foods and their raw materials, particularly from oxidative and microbial spoilage and also to extend their shelf-life characteristics. Increased use of synthetic packaging films has led to serious ecological problems due to their total non-biodegradability. Continuous awareness by one and all towards environmental pollution by the latter and as a result of the need for a safe, eco-friendly atmosphere has led to a paradigm shift on the use of biodegradable materials, especially from renewable agriculture feedstock and marine food processing industry wastes [4]. Packaging material derived from sustainable resources is now receiving considerable interest, because of the growing public awareness of environmental issues and the advantages in product marketing. Low oxygen permeability can be a key requirement for food packaging material in addition to good mechanical properties in terms of high strength and flexibility. Hemicellulose derived packaging materials have been produced with oxygen permeability values that compare favorable with those of other biopolymers such as amylase, amylopectin and chitosan [5].Thus, the purpose of this research was to characterize the properties of films from sugarcane bagasse hemicellulose which extracted using alkali extraction method with addition of different volume of ethanol.

2. Material and methods

2.1. Material

Sugarcane bagasse was obtained from local night market in Shah Alam, Malaysia. The samples were dried at 60 °C and ground to1.0 mm size prior to use.

2.2. Alkali extraction

Alkali extraction method was used with some modifications to extract hemicelluloses from sugarcane bagasse [1]. Extraction was done with 1:25 ratio sugarcane bagasse to solvent of 0.5M NaOH. The mixtures were stirred at 55.0°C, 400 rpm for 2 hours. After filtration, the supernatant were adjusted with 6M hydrochloric acid, HCl to pH 5.5. Next, the mixtures were kept at 4.0 °C for 24 hours. After 24hours, the mixtures were centrifuged at 3500 rpm for 15 minutes. The suspension was filtered and then the supernatant was added with different volumes of ethanol. There were 4 types of ethanol volume that were used in this step which were 85mL of cold ethanol solution containing 10% acetic acid (A), 85 mL of cold ethanol solution (B), 4 volumes of ethanol solution (C) and 2 volume of ethanol solution with 0.2 volume acetic acid (D) to precipitate the hemicelluloses. Later, the mixtures were centrifuged at 3500rpm for 20 minutes to obtain the pellet. The pellet were dried at 40.0°C for 24 hours and used as xylan source.

2.3. Film preparation

Hemicelluloses films were prepared with some modifications [6]. The hemicelluloses from all extracts were dissolved in distilled water to forming the solution with concentrations of 10.0% (w/v). Then, the solution was stirred at room temperature for 8 hours with magnetic stirrer. Next, the films solutions were casted and dried in controlled environment at 40.0°C for 1 hour and then placed in a desiccator for 24 hours. After 24 hours, films were conditioned at 52.9% RH using saturated magnesium nitrate, at 25.0°C for 48 hours prior to all analysis.

2.4. Thickness Measurement

The film thickness was measured by using a thickness gauge (Mitutoyo, Kawasaki, Japan). The measurements were taken at 5 different places on the films, and the average value was calculated.

2.5. Solubility

The film was cut and dried in an oven at 70.0°C to constant weight. The film was weighed to obtain the initial film dry weight. Then, 0.05 g of the film were put into 10 g of distilled water for I hour. The remaining pieces of film was taken and dried at 70.0°C for 24 hours and weighed to obtain the final weight. The solubility (%) value was calculated as follows:

$$\text{Solubility (\%)} = \frac{\text{Initial weight-Final weight}}{\text{Initial weight}} \times 100 \quad (1)$$

2.6. Water Vapor Transfer Rate (WVTR)

The WVTR tests was determined with some modifications [8]. The films were prepared in triplicates and tests at 25.0 ± 2 ºC. The tests films were sealed to a glass permeation cell containing silica gel with a 1.5 cm headspace and placed in a dessicator maintained at 52.9 % using saturated salt solution of $Mg(NO_3)_2$. The dull sides of the films were oriented towards the higher RH compartment. The cups were weighed to the nearest 0.001 g at 24 hours intervals for 3 days. The water vapor transmission rate through the films was determined from weight loss of the cup over time (Appendix F). Net weight (grams) versus time (hours) plots were obtained. The WVTR values of the films were calculated as follow:

$$WVTR = [slope\ (g/h) \times (24\ h/day)] / area\ of\ the\ films\ (m^2)$$

2.7. Mechanical Properties

The tensile strength and breaking elongation of films were measured using a TA.XT2TM Texture Analyzer (Stable Micro System, Surrey, UK) according to ASTM Standard Method D882-88 (ASTM, 1989a). The films strips were stretched (each measuring 20 mm x 5 mm) at load 10 N.

2.8. Color Measurement

The film color was determined by using a colorimeter (CM-3500D Minolta spectrophotometer, Minolta, Japan) calibrate with CM-A124 zero calibration box and CM-A124 white calibration plate. The Hunterlab color scale was used, lightness = 0 to 100 (Black and white) and chromaticity parameters, +a is the red direction, -a is green direction, +b is the yellow direction and -b is the blue direction. The samples were analyzed in triplicates.

2.9. Statistical Analysis

The experimental results were expressed as mean ± S.D (standard deviation). One way ANOVA was used to analyse the experimental data and Duncan's multiple range test was applied to determine the significantly different ($P<0.05$) samples. The SPSS (Statistical Package for Social Science) statistical computer package was used to analyze the experimental data (SPSS, Inc., Chicago, IL, USA).

3. Results and discussion

3.1 Hemicelluloses yield and lignin content

The effect of different volume of ethanol on the hemicelluloses yield was shown in Fig. 1. The highest yield of hemicelluloses was obtained when 85 mL of cold ethanol solution was added to the supernatant. The result also showed that the lignin content increased when the hemicelluloses yield increased and the lignin content decreased when hemicelluloses yield decreased. This result indicates that lignin-hemicellulosic complex was co-extracted at different volume of ethanol used, and the lignin content also depends to the hemicelluloses yield.

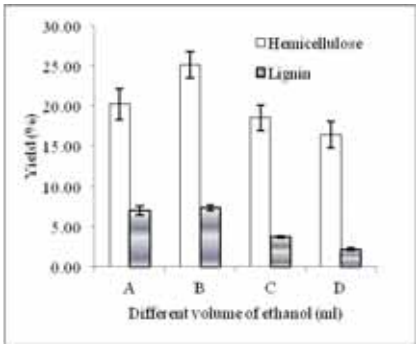

Fig. 1. Hemicellulose yield and lignin content of the extract. 85mL of cold ethanol solution containing 10% acetic acid (A), 85 mL of cold ethanol solution (B), 4 volumes of ethanol solution (C) and 2 volume of ethanol solution with 0.2 volume acetic acid (D).

3.1. Film thickness, solubility and water vapor transfer rate (WVTR)

Film thickness prepared by hemicelluloses A, B, C and D showed no significant difference with an average thickness of 0.15mm, 0.13mm, 0.14mm and 0.15mm, respectively as shown in Fig.1. The film thicknesses of cotton stalk xylan were reported in the range of 0.29 – 0.38 mm while hemicelluloses film from oil palm frond showed no significant difference with an average thickness of 0.13 mm – 0.14 mm [6-7]. Percent solubility of the films A, B, C and D are 36.9 %, 45.2 %, 61.9 % and 67.1 %, respectively as shown in Table 1. Hemicellulose film A has the lowest solubility in water might be due to their high percentage of lignin content as compared to hemicelluloses film D (Fig. 1), since lignin has low solubility in water. There was no significant difference between the solubility of the film in water with respect to xylan concentration whereas about 99 %, indicating that the films were almost totally soluble in water [6].

Table 1. Thickness, solubility and WVTR of hemicelluloses films

Hemicelluloses film	Thickness (mm)	Solubility (%)	WVTR (g/m^2.day)
A	0.15 ± 0.01^a	36.9 ± 1.31^a	250.4 ± 11.21^a
B	0.13 ± 0.01^a	45.2 ± 1.46^b	352.6 ± 17.52^b
C	0.14 ± 0.01^a	61.9 ± 1.50^c	406.4 ± 10.82^c
D	0.15 ± 0.01^a	67.1 ± 0.67^d	483.3 ± 8.24^d

Data are means ± standard deviations for n = 3. Thickness, solubility and WVTR of hemicelluloses films that have different superscripts are significantly different ($P < 0.05$) according to Duncan's multiple test range.

As shown in Table 1 above, the WVTR for hemicelluloses film A is the lowest which is 250.4 $g/(m^2.day)$ whereas WVTR for hemicelluloses film D is the highest which is 483.3 $g/(m^2.day)$. The WVTR has potential for food-packaging films and depends on the type of the material to be packaged and the storage conditions. Film A is the lowest WVTR probably because of high lignin content in the hemicelluloses films. High WVTR is beneficial for potential in packaging material that used for vegetables or fruit packaging purposes. It is considering the continuation of respiration and some of the metabolic activities. The WVTR for all hemicelluloses films prepared were higher as compared to gluten-xylan composite film [8].

3.2. Tensile strength of hemicelluloses films

Tensile strength expresses the maximum stress developed in a film during a tensile test and offers a measure of integrity and heavy-duty use potential of films [9]. As shown in Fig. 2 all the films break at below 2.0 MPa without any elongation.

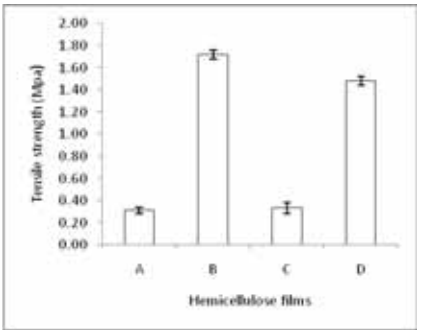

Fig. 2. Tensile strength of hemicelluloses film A, B, C and D. 85mL of cold ethanol solution containing 10% acetic acid (A), 85 mL of cold ethanol solution (B), 4 volumes of ethanol solution (C) and 2 volume of ethanol solution with 0.2 volume acetic acid (D)

Hemicelluloses film B has a highest tensile strength as compared to the other films. The differences in tensile strength for each film probably were depends on the ratio of ethanol and acetic acid added to the sample. The value of the tensile strength of the sugarcane bagasse hemicelluloses films were compared to the hemicelluloses films from cotton waste, oil palm fronds and barley husk which were 1.3 MPa, 10.0 MPa and 50 MPa, respectively [6-7,10]. Mechanical properties changed not only due to different process conditions, but also due to type and composition of hemicelluloses [8].

3.3. Colour of hemicelluloses films

The colour is an important property for the potential applications in packaging of light-sensitive materials. Colour readings of the films were carried out at room temperature on 4 types of films. The L* value represent "lightness", which is from zero (black) to 100 (white) and chromaticity parameters, +a is the red direction, -a is green direction, +b is the yellow direction and –b is the blue direction. The color of the hemicelluloses film A was darker compared to other film probably due to high lignin content proved by smaller value of L* which was 36.30, whereas film B, film C and film D were lighter in colour which was have value above 50 (Table 2). The colour of the oil palm frond hemicelluloses films from previous study also shown with dark colour [7]. The differences in colour for each film were probably attributed by different sources and methods of hemicellulose extracted because the colour of the film is depend on the lignin content. High percentages of lignin content will contribute to the dark colour of the hemicelluloses films.

Table 2. Color measurement of hemicelluloses films

Hemicelluloses film	L*	a*	b*
A	36.30 ± 0.95	5.56 ± 0.27	23.27 ± 0.75
B	58.73 ± 0.51	-1.04 ± 0.03	11.68 ± 0.19
C	58.74 ± 0.04	-3.10 ± 0.02	15.12 ± 0.02
D	60.47 ± 0.02	-3.15 ± 0.02	4.17 ± 0.02

85mL of cold ethanol solution containing 10% acetic acid (A), 85 mL of cold ethanol solution (B), 4 volumes of ethanol solution (C) and 2 volume of ethanol solution with 0.2 volume acetic acid (D).

4. Conclusion

This study showed that all hemicelluloses films produced a self-supporting film with different properties and also hemicellulose from sugarcane bagasse has a potential for production of biodegradable films.

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